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Research Article

Thermogravimetric Analysis as a High-Throughput Lignocellulosic Biomass Characterization Method

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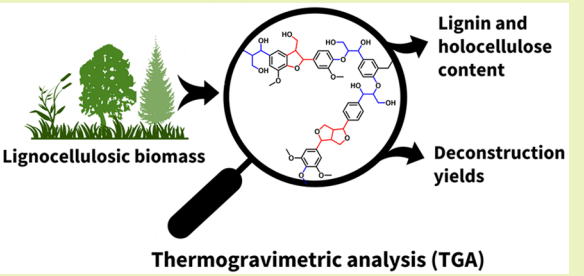
ABSTRACT: The characterization of lignocellulosic biomass is essential to unlocking the promise of lignocellulosic biorefineries through facilitated feedstock selection, optimized valorization strategies, minimized costs, and reduced environmental impacts. Although current characterization approaches are accurate and consistent on a laboratory scale, such "wet-laboratory" methods are time and labor intensive, with a low sample throughput and limited scale-up potential. Herein, we report the development of a rapid and efficient characterization strategy for whole lignocellulosic biomass using thermogravimetric analysis (TGA). We demonstrate that this TGA approach achieves accuracy and repeatability comparable to that of the standard procedure from the National Renewable Energy Laboratory (NREL). In comparison to the NREL procedure, the TGA characterization method requires a fraction of the experimental time and sample quantity and minimizes the volume of chemical reagents needed and waste generated. We also leverage this TGA approach to predict the yields of phenolic products obtained from whole biomass deconstruction via reactive distillation-reductive catalytic fractionation. As such, TGA is demonstrated as a powerful lignocellulosic biomass characterization tool with broad applicability in biorefining.



KEYWORDS: *thermogravimetric analysis, lignocellulosic biomass, biomass characterization, lignin, reductive catalysis, high-throughput, phenolic yield, holocellulose*

INTRODUCTION

Lignocellulosic biomass (LCB) holds incredible promise as an alternative feedstock to petroleum for the production of materials, chemicals, and fuels.[1−8] In this regard, the rapid and accurate characterization of LCB is a critical step for biorefining because it enables biorefineries to quickly screen feedstocks, predict and manage biorefinery outputs, and optimize overall plant economics while minimizing environmental impacts.[2,9] LCB characterization primarily involves the quantification of three major components—cellulose (40−60 wt %), hemicellulose (10−40 wt %), and lignin (15−30 wt %).[10] Cellulose is a crystalline polymer composed of glucose monomers, whereas hemicellulose is an amorphous polymer composed of hexoses and pentoses. Lignin is a polymeric network of syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) aromatic moieties connected by C−O bonds (e.g., *β*-O-4 linkages) and C−C bonds (e.g., *β*−*β*, 5−5, *β*-5, and *β*-1 linkages).[11,12] The content of both lignin and holocellulose (i.e., the carbohydrate fraction of the biomass including cellulose and hemicellulose) and S/G/H ratios vary considerably by plant species, tissue, and age.[9,13,14] This inherent complexity across biomass feedstocks necessitates robust and adaptive characterization strategies.

As biorefineries scale up, high-throughput characterization methods (i.e., methods capable of rapidly screening a large number of samples) are needed to meet the increased volume of feedstocks, but current approaches are limited by intensive "wet-laboratory" (i.e., manual chemistry involving liquid reagents) procedures or low repeatability to meet biorefinery demands.[1,2,15−17] The standard method for LCB characterization is a laboratory analytical procedure developed by the National Renewable Energy Laboratory (NREL).[15,18] The NREL procedure quantifies holocellulose by hydrolyzing it into monomeric sugars and analyzing the sugars via high-performance liquid chromatography and measures lignin via the Klason method, which is a gravimetric analysis approach.[18] The procedure is accurate for evaluating holocellulose and lignin content in a range of woody biomass samples (i.e., hardwoods and softwoods).[15,18] However, the lignin is particularly challenging to characterize consistently because of its inherent complexity, and the NREL procedure also has increased error associated with feedstocks or feedstock components that contain higher levels of nonstructural

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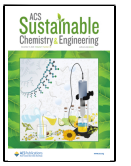

components (e.g., proteins, waxes, suberin), such as in herbaceous (grassy) feedstocks.[2,15,16] Furthermore, the NREL method's throughput is limited by its labor-intensive procedure, its accuracy is constrained by the analytical skills of the researcher(s) performing the characterizations, and its analysis provides limited structural information beyond the component abundances.[2]

Thermogravimetric analysis (TGA) can be leveraged as a higher-throughput alternative to the NREL method in which the components of complex mixtures and materials are resolved by their distinct thermal degradation "fingerprints".[19] TGA experiments can be set up in as little as a few minutes and concluded in under 2 h, which is a significant time savings versus the traditional "wet-laboratory" techniques, especially with respect to active labor for researchers. Additionally, TGA requires only ∼5−10 mg of sample, uses minimal chemical reagents, provides greater consistency by eliminating human variability/error, and can be leveraged to provide information about the LCB sample's thermal stability. TGA is commonly used to study the kinetics of LCB pyrolysis and has been previously applied to predict cellulose, hemicellulose, and lignin contents.[20−26] Although the cellulose and hemicellulose measurements are consistent, the lignin measurements from previous TGA procedures are not repeatable with high confidence because these methods are built upon kinetic parameters (e.g., activation energy) that vary significantly between samples.[20−26] For example, Anca-Couce et al. found significant deviations in lignin activation energies in pyrolysis-based methods, even between researchers using the same biomass feedstocks and TGA procedures.[20] Another limitation of the pyrolysis-based approaches is that additional experiments are required to account for the remaining char content at the end of TGA runs.[27] Other TGA characterization protocols can consistently determine the lignin content in a specific species but have not been generalized to multiple species of diverse LCB feedstocks.[28−30] Furthermore, some TGA approaches require the biomass to be fractionated prior to analysis, disrupting the chemical structure of the components prior to measurement and limiting the potential throughput by including labor-intensive steps.[17,31] Because TGA inherently measures the thermal stability of a sample, TGA also has been employed to predict technical lignin phenolic deconstruction yields in a reactive distillation-reductive catalytic deconstruction (RD-RCD) reaction.[32] That work indicated that more recalcitrant lignins had both lower deconstruction yields and higher degradation temperatures; although, that approach was not extended to more complex, whole LCB feedstocks.[32] Deconstruction yields of whole biomass have previously been predicted by the fraction of β-O-4 bonds, which can be measured via ^{31}P-, ^{19}F-, and heteronuclear single-quantum coherence nuclear magnetic resonance spectroscopy techniques.[11,31,33−36] However, these spectroscopic approaches either cannot provide absolute quantifications due to differences in backbone and pendant/end-group relaxation times or require fractionation and chemical functionalization prior to analysis, thus limiting their throughput and ultimate biorefinery applicability.[2,11,31,33,34]

Herein, we report a higher-throughput TGA characterization method to measure lignin, hemicellulose, cellulose, and holocellulose contents and predict deconstruction yields from whole LCB. We applied a computational approach to separate LCB thermal degradation peaks and leveraged this analysis to quantify holocellulose and lignin abundances directly from unfractionated biomass. Ten diverse LCB feedstocks were chosen to design and validate the model, including three native hardwoods, three native softwoods, three native herbaceous sources, and one hybrid hardwood. We aimed to achieve an accuracy and repeatability comparable to that of the NREL procedure. Finally, we leveraged the TGA approach to develop a screening method for whole LCB that enables the prediction of reactive distillation-reductive catalytic fractionation (RD-RCF) phenolic bio-oil yields based on the thermal stability of the lignin component in native biomass. Thus, we have developed a higher-throughput TGA characterization method for whole LCB and demonstrated its extended applicability in biorefining by using the thermal degradation characteristics of feedstocks to predict deconstruction performance.

MATERIALS AND METHODS

Materials. Ethyl acetate (>99.5%), hexanes (>98.5%), methanol (>99.9%), glycerin (ACS grade), 2 wt % ruthenium on 3.18 mm alumina pellets (Ru/Al_2O_3), magnesium sulfate, xylan from corn core, cellulose (laboratory grade), and lignin (dealkaline) were purchased from Fisher Scientific. Ethanol (200 proof, anhydrous) was purchased from Decon Laboratories. Helium (grade 5), nitrogen (grade 5), and compressed air (grade 5) were purchased from Keen Compressed Gas. All chemicals were used as received. Hybrid poplar, lodgepole pine, corn stover, wheat straw, sugarcane bagasse, eucalyptus, juniper, and maple were provided by the Bioenergy Feedstock Library at Idaho National Laboratory. Alder and douglas fir were purchased from Forest Concepts, LLC. Additional biomass feedstock composition information is provided in Tables S1 and S2.

TGA Experiments. Prior to TGA experiments, feedstocks were processed to remove extractives according to previously reported procedures.[15,37] Extractive removal is necessary to reduce noise in derivative thermogravimetric curves and avoid overestimation of the holocellulose content, especially for herbaceous samples. Briefly, samples were sonicated for 10 min at least four times in 80 vol % ethanol/20 vol % deionized water followed by sonication in hexanes at least twice. Extractive-free samples were dried overnight (∼16 h) at 40 °C under a dynamic vacuum. TGA was conducted on a Discovery TGA5500 instrument under an airflow of 20 mL/min. Relatively small masses of biomass samples (3 ± 2 mg) were loaded onto clean, tared 100 μL platinum TGA pans without lids (TA Instruments or DSC Consumables). The samples were heated to 125 °C at a rate of 25 °C/min, held at 125 °C for 25 min to remove residual moisture, cooled to 50 °C, and heated from 50 to 700 °C at a rate of 20 °C/min. TGA curves were analyzed with the Trios software (TA Instruments). Curves were smoothed and derivatives were calculated via a least-squares moving window technique with the window size set to five data points. The TGA lignin, hemicellulose, and cellulose quantification model was implemented in MATLAB 2021b (MathWorks). Additional details are provided in the method development sections, and the complete MATLAB code is linked in the Supporting Information.

Reactive Distillation-Reductive Catalytic Fractionation. RD-RCF was conducted according to the published literature.[32] LCB (2−4 g), glycerin (125 mL), and Ru/Al_2O_3 pellets (2:1 lignin-to-catalyst weight ratio) were loaded into a 250 mL round-bottom flask equipped with a Teflon magnetic stir bar. The round-bottom flask was connected to the receiving flask with a distillation adaptor and an elbow with a vacuum takeoff. The flask was set in a DrySyn block on an IKA RCT Basic hot plate with a PT.1000 thermocouple and wrapped in a fiberglass blanket for insulation. The reactor was heated to 250 °C and stirred at 650 rpm for 24 h before cooling to room temperature (∼20 °C). The distillate was extracted with ethyl acetate, washed with brine, and dried over magnesium sulfate. The ethyl acetate was thoroughly removed by evaporation under vacuum using an automated Buchi R-300 system, and then the pressure was reduced

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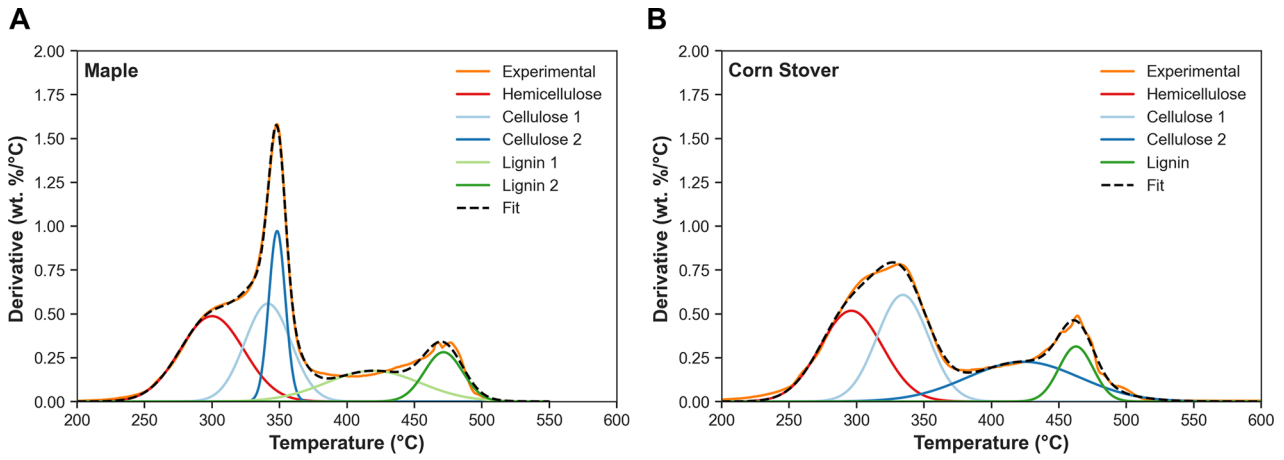

Figure 1. DTG curves fit with Gaussian curves in the TGA characterization model for (A) maple, a woody biomass, and (B) corn stover, an herbaceous biomass. The first derivative curve of the experimental data is shown in orange, the model hemicellulose curve is in red, the model cellulose curves are in blue, the model lignin curve(s) are in green, and the summative model fit is the dashed black line.

further (<80 mbar at 50 °C) for several minutes to ensure that samples were fully dried to yield a yellow-to-brown colored bio-oil.

RD-RCF Product Analysis. RD-RCF bio-oils were dissolved in methanol and subsequently analyzed via gas chromatography−mass spectrometry (GC−MS). GC−MS was conducted on a Shimadzu QP2020 NX instrument (Shimadzu Corporation) equipped with an MS detector, a flame ionization detector, an AOC-20i autosampler, and an Rtx-5MS column with helium as the carrier gas. The injector temperature was set to 300 °C with a split ratio of 10:1. The initial oven temperature was set to 50 °C, and the oven temperature was held at 50 °C for 1 min before ramping up to 315 °C at a rate of 15 °C/min. The MS interface temperature was set to 250 °C with an ion source temperature of 230 °C. GC−MS chromatograms were analyzed using Shimadzu GCMSsolution software, and products were identified using the National Institute of Standards and Technology (NIST) MS library. The mass of phenolic products was calculated as the fraction of relative peak areas corresponding to phenolic products in the total mass of bio-oil distillate,[32,38] and phenolic yields were calculated on a lignin dry weight basis (i.e., the mass of phenolic products divided by the mass of lignin in the starting dry biomass). This semi-quantitative method was validated in previous work.[32]

RESULTS AND DISCUSSION

TGA Characterization Method Development. Differential thermogravimetric (DTG) curves are commonly used to locate distinct thermal degradation events. Literature has established the decomposition temperature ranges for hemicellulose, cellulose, and lignin, approximately 250−300, 300−350, and 300−500 °C, for each component, respectively.[21,39] Hemicellulose degrades at the lowest temperatures in a broad peak because of its amorphous structure, and cellulose degrades next as a sharp peak due to the polymer's homogeneity and crystallinity.[21,39] Lignin degrades last across a wide temperature range, and its degradation pattern is highly variable between feedstocks largely impacted by the distributions of C−O and C−C bonds between monolignol subunits and differences in S/G/H ratios.[21,39] However, these degradation windows overlap, especially in an inert atmosphere, in which most of the previously reported TGA characterization studies are conducted, because they were focused on biomass pyrolysis.[20−27] TGA in an oxidative environment (i.e., under air) significantly improves separation between the holocellulose and lignin degradative events, and this improvement in resolution is shown for the hybrid poplar in Figure S1. TGA curves for each of the individual components are shown in Figure S2. Gaussian distributions were fit to the DTG curves to capture the component decomposition behavior for woody feedstocks (Figure 1A) and herbaceous biomass (Figure 1B). Representative curves for the remaining eight biomass samples are shown in Figures S3−S10, along with more information on the initial "guess" and final model variable values (Table S3). To capture the hemicellulose and cellulose decomposition behavior, one and two Gaussians were fit to the DTG curve, respectively. For woody biomass, two Gaussians were used to capture the lignin decomposition behavior: the lower and higher temperature curves likely correlate to the relative abundances of more labile C−O linkages versus more recalcitrant C−C linkages. For herbaceous biomass, lignin degradation does not appear to follow the two-step degradation pattern, and the behavior was best captured using a single Gaussian.

The lignin, hemicellulose, cellulose, and holocellulose quantification method was implemented in MATLAB, and the optimization routine is outlined in Figure 2. The model relies on an initial "guess" of three input variables for each Gaussian: μ (mean/peak temperature), σ (standard deviation/width), and a (weight factor/peak height). The initial values for each variable were chosen empirically for each feedstock to qualitatively fit each curve to its corresponding thermal decomposition event (Table S3). The model used the initial guess and DTG data to determine a fit function as the sum of the Gaussians at each temperature point. The root-mean-square error (RMSE) between the fit function and the experimental data at each point was minimized using the fmincon function in MATLAB, a gradient-based nonlinear programming solver.[40] The model calculated the area under each curve, corresponding to the lignin, hemicellulose, and cellulose weight percentages, measured on an extractive-free, dry-weight basis. The holocellulose is calculated as the sum of the hemicellulose and cellulose areas. The complete MATLAB model code is accessible through a link in the Supporting Information.

TGA Characterization Method Validation. Parity plots for the abundance of lignin, holocellulose, hemicellulose, and cellulose in each LCB feedstock measured by the NREL and TGA characterization methods are shown in Figure 3A,B and Figure S11A,B, respectively. The relative standard deviation

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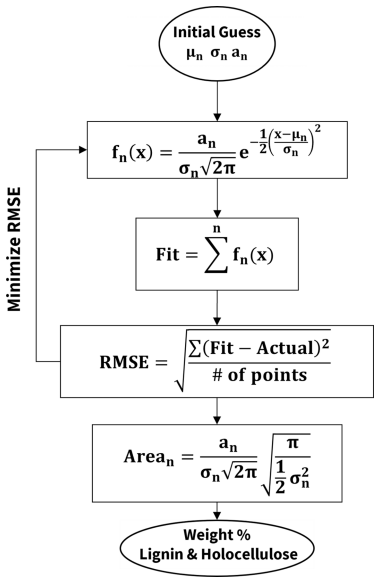

Figure 2. Model optimization routine performed in MATLAB. The ovals highlight the model inputs and outputs. The boxes show the intermediate model iterations and calculations. For woody biomass, n = 5, and for herbaceous biomass, n = 4. In the function, μ_n is the mean, σ_n is the standard deviation, and a_n is the weight factor.

(RSD) for lignin content using the TGA method is 3.7 wt %, and the RSD for holocellulose content is 1.7 wt %, indicating that the TGA approach is repeatable. For hemicellulose, the RSD is 18.0 wt %, and for cellulose, the RSD is 6.3 wt %; although the standard deviations are high individually for hemicellulose and cellulose, their values when summed for the holocellulose measurement are much more consistent as indicated above. The NREL procedure reports method uncertainties for each component with an RSD of 1.8 wt % for lignin, 1.6 wt % for glucan, and 1.8 wt % for xylan;[41] however, these statistics were calculated for 154 samples of homogenized corn stover in 13 batches, by seven analysts in two laboratories.[41] Another study has shown RSDs of 1.7 to 2.8 wt % for lignin repeatability and 4.6 to 12.6 wt % in terms of reproducibility between laboratories, values that likely are more representative when the method is applied broadly.[42] For holocellulose components, the uncertainties generally were <5 wt % for intra-laboratory variability and <10 wt % for variability between laboratories.[42] Other recent publications have reported values measured via the NREL procedure with RSDs >10 wt %.[9,43] Given this variability in reporting and that the TGA approach is a higher-throughput screening method, the target repeatability for the approach was chosen to be <5 wt % RSD. For both lignin and holocellulose, this target was easily achieved. Thus, the TGA characterization method achieves comparable repeatability to the NREL procedure for the measurement of lignin and holocellulose content.

The parity plots also emphasize the similarity between measurements made with the TGA method versus the NREL procedure. There is good agreement between the lignin quantities measured via the NREL procedure and the TGA approach for both woody and herbaceous biomass. The RMSE value is 3.7 wt % for woody, herbaceous, and all biomass, respectively, and the mean absolute error (MAE) values are 2.5, 3.6, and 2.9 wt % for woody, herbaceous, and all biomass, respectively. RMSE more heavily penalizes outliers, whereas MAE treats all samples equally.[46] For both metrics, a lower value indicates a lower error and thus a more robust and accurate model. Therefore, the RMSE and MAE values indicate that the TGA and NREL approaches are comparable, especially in the case of woody biomass. The holocellulose values shown in Figure 3B are the sum of the corrected hemicellulose and cellulose amounts. The RMSE values of 4.3, 1.1, and 3.3 wt % and MAE values of 4.0, 0.9, and 2.7 wt % were achieved for woody, herbaceous, and all biomass, respectively. These values demonstrate excellent agreement between the two measurement approaches for holocellulose.

The TGA method consistently underestimates the hemicellulose content and overestimates the cellulose content in comparison to the NREL procedure, so empirical correction factors were generated to account for these under- and overestimations, respectively. The correction factors were

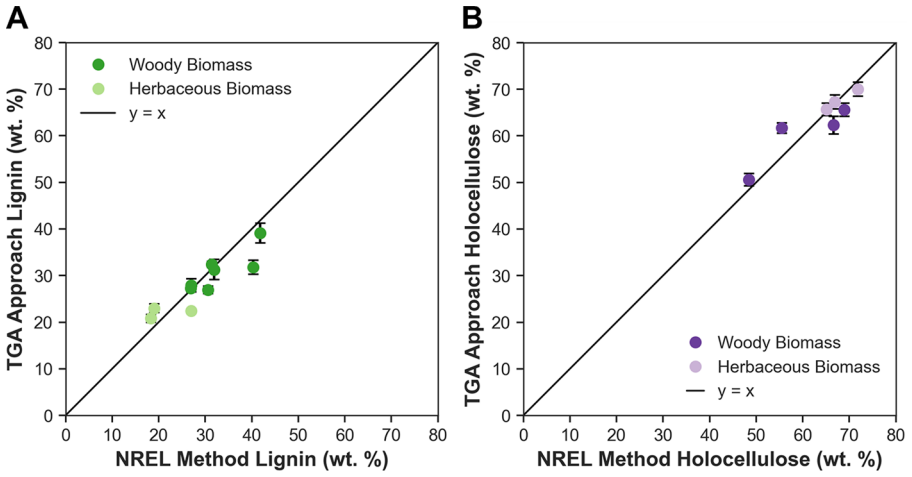

Figure 3. Parity plots for TGA and NREL characterization methods for (A) lignin and (B) holocellulose (i.e., hemicellulose and cellulose). A diverse set of 10 LCB feedstocks were characterized by both approaches. The TGA samples were measured in replicates of five, and the error bars represent the standard deviations. The NREL method values were reported or measured in triplicate, and the error bars represent the standard error of the method (0.5 wt % for lignin, hemicellulose, cellulose, and holocellulose).[44,45] The holocellulose plot shows the sum of the corrected hemicellulose and cellulose values for each biomass. Parity plots for hemicellulose and cellulose and raw data for the plots are included in Figure S11 and Table S4.

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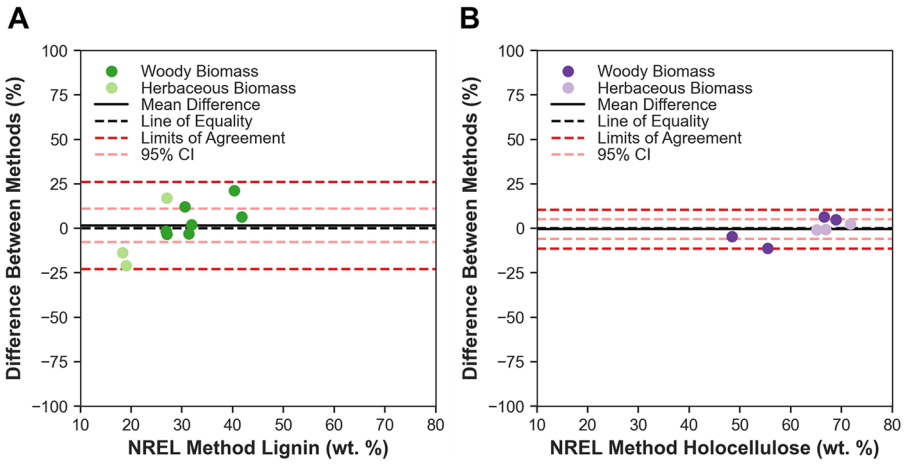

Figure 4. Krouwer plots for the TGA and NREL characterization methods for (A) lignin and (B) holocellulose (calculated from the sum of the corrected hemicellulose and cellulose values). The relative difference between methods is calculated as the difference between the NREL method value and the TGA method value, normalized to the NREL method value. The mean difference is shown as a solid black line; the line of equality is the black dashed line; the upper and lower limits of agreement (1.96 × the average standard deviation of the difference) are the dashed pink lines; and the 95% CI of the difference are the dashed red lines.

calculated using Microsoft Excel's solver to minimize the RMSE between the TGA and NREL methods for each component. For hemicellulose, the correction factor (b) is −4.1, and for cellulose, the correction factor is 9.3, indicating that the TGA approach consistently underestimates the hemicellulose by 4.1 wt % and overestimates the cellulose by 9.3 wt %. The discrepancy between hemicellulose values could result from the broad thermal degradation of hemicellulose (because of its heterogeneous composition) that is not fully captured by the hemicellulose curve. The discrepancy between cellulose values likely is from residual extractives or other nonstructural components (e.g., proteins) degrading in the same temperature range as cellulose.[15,18] Future work could investigate whether a more extensive extractive removal procedure in the sample preparation, including additional washes and/or solvents, reduces the differences between the cellulose quantification approaches. With the correction factors, relatively good agreement between the TGA and NREL methods is achieved with RMSE values of 6.0 and 8.4 wt % and MAE values of 4.5 and 6.2 wt % for hemicellulose and cellulose, respectively. These corrected values were summed to calculate the holocellulose content, which achieved better agreement between methods than either the hemicellulose or cellulose contents individually.

In addition to the parity plots, the Krouwer plots in Figure 4A,B further emphasize the similarity between lignin and holocellulose measurements made with the TGA approach versus the NREL procedure. The Krouwer plots are difference plots that capture the agreement between two measurement methods and determine if bias exists between them, with the conventional standard method plotted on the x-axis as the reference.[47] The bias is significant if the line of equality is not within the 95% confidence interval (CI); herein, the line of equality is well within the 95% CI for both lignin and holocellulose.[47] For lignin and holocellulose, all of the points are within the limits of the 95% CI, and most points are within or equal to the limits of agreement. Together with the parity plots, the Krouwer plots suggest agreement between the two measurement methods. It is also important to note that although the NREL method is the conventional standard for LCB characterization, an unambiguous, "correct" measurement method, particularly for lignin content, does not exist, and thus, consistency between measurements is critical as it enables the relative comparison between feedstocks and samples.[16]

The TGA characterization method requires only ∼10 mg of sample to run in triplicate, whereas the NREL procedure requires ∼1 g of sample. Furthermore, the TGA approach requires no additional chemical reagents and generates no waste beyond those used in the sample preparation (i.e., extractive removal and drying required by both methods). The removal of extractives necessitates some wet chemistry; however, extractive removal takes a small fraction of the time, labor, and chemical reagents in comparison to the entire NREL procedure. Furthermore, extractives can be removed in bulk for all replicates of a sample, and it is often already done in biorefinery systems as a preprocessing step.[2,48] In addition to the structural components measured and discussed above, the same procedure can be used to measure the moisture and ash contents of the biomass samples; those values are reported in Tables S1 and S3, respectively. The TGA approach can be completed in ∼2 h, while the NREL method takes 3 days from start to finish. These time and resource savings, in combination with comparable accuracy and consistency, highlight the potential of TGA as a higher-throughput LCB characterization method.

Screening RD-RCF Yields by Thermal Stability. Literature has shown an inverse correlation between the thermal stability of technical lignin and phenolic RD-RCD yields.[32] This correlation results from more recalcitrant lignin (i.e., lignin with a higher C−C/C−O bond ratio) having lower deconstruction yields and increased thermal stability (i.e., higher degradation temperatures). Herein, it was hypothesized that a similar correlation existed between the thermal stability of whole native biomass and the RD-RCF yields. Note: fractionation refers to the separation of mixture constituents into individual components or submixtures (e.g., RCF from whole biomass); deconstruction refers to the breakdown of materials into smaller fragments (e.g., RCD of technical lignin).[2] The RD-RCF method used in this study concurrently fractionates the biomass and deconstructs the lignin. The relationship between catalytic deconstruction yields and the thermal stability for the 10 LCB feedstocks studied in this work

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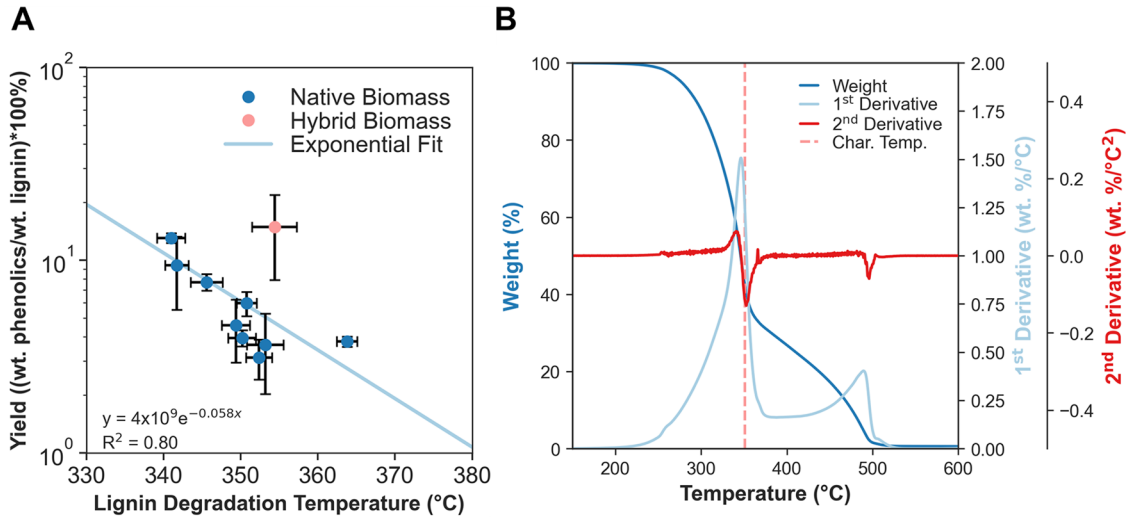

Figure 5. Relationship between lignin's thermal stability and phenolic RD-RCF yield. (A) Characteristic lignin degradation temperature vs phenolic yield plotted on a semi-log plot with an exponential fit (R^2 = 0.80). (B) Identification of the lignin degradation temperature for lodgepole pine. The normalized weight loss (blue), first-derivative (light blue), and second-derivative (red) curves are shown as functions of temperature. The second-derivative curve was smoothed via a least-squares moving window technique. The characteristic temperature is the minimum of the second derivative curve, highlighted by the dashed pink vertical line. Raw data for Figure 5A are included in Table S6.

is shown in Figure 5A. Additional information on RD-RCF product analysis and RD-RCF bio-oil chromatograms for each biomass are supplied in Figures S12−S22 and Table S5. The characteristic lignin degradation temperature was determined to be the minimum of the second-derivative curve (Figure 5B). This point corresponds to the onset of lignin degradation and the inflection point between the holocellulose and lignin degradation events. The native biomass data were exponentially fit with an R^2 value of 0.80. A nonlinear fit was anticipated, as the production of one phenolic unit requires the cleavage of two interunit linkages (one on either side).[11] The genetically modified feedstock (i.e., hybrid poplar) was not included in the analysis because it had a significantly higher yield than would be expected given its high degradation temperature. A previous study has shown that the genetic modification of poplar affects both the lignin structure and the reactivity of the lignin. Therefore, the hybrid poplar is not expected to follow the same trend as the native biomass.[49] The strong relationships between the characteristic lignin degradation temperatures and phenolic yields in the native biomass highlight the potential to screen LCB feedstocks by TGA. The RD-RCF phenolic yields in this study were relatively low, likely due to catalyst choice/loading or mass/heat transfer limitations from a low stir rate.[50] However, it is suspected that an exponential trend likely can be identified between the thermal stability of lignin and the phenolic yields under any consistent set of reaction conditions. Predicting phenolic yields directly from the TGA curves of whole LCB biomass has enormous potential to enable lignocellulosic biorefineries to quickly choose feedstocks or screen biomass lots for quality assurance.

CONCLUSIONS

A rapid and robust whole LCB characterization method was developed that leverages TGA to quantify lignin, hemicellulose, cellulose, and holocellulose abundance and predict phenolic deconstruction yields. This TGA method enables the repeatable measurement of the lignin and holocellulose contents. Notably, the approach achieved results comparable to those of the NREL method, which is the current standard LCB characterization protocol. Additionally, the TGA approach led to significant reductions in the experimental time, biomass sample input, and required reagent volumes. The TGA characterization method also was employed to predict phenolic yields from whole biomass subjected to reductive catalytic fractionation. The approach utilized relationships linking the lignin degradation onset temperature to predict deconstruction yields. With the potential for broad applicability in biorefining, the advantages of using TGA as a higher-throughput LCB characterization approach have been demonstrated.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c03769.

Biomass composition information, effect of the TGA atmosphere on LCB decomposition behavior, representative DTG curves with fitted Gaussians for each feedstock, RD-RCF product analysis, lignin degradation temperature and phenolic yield data by biomass, and link to the MATLAB code (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS:

(CI)	confidence interval
(DTG)	differential thermogravimetric
(G)	guaiacyl
(GC−MS)	gas chromatography−mass spectroscopy
(H)	*p*-hydroxyphenyl
(HSQC)	heteronuclear single quantum coherence
(LAP)	laboratory analytical procedure
(LCB)	lignocellulosic biomass
(MAE)	mean absolute error
(NREL)	National Renewable Energy Laboratory
(RD-RCD)	reactive distillation-reductive catalytic deconstruction
(RD-RCF)	reactive distillation-reductive catalytic fractionation
(RMSE)	root-mean-square error
(S)	syringyl
(TGA)	thermogravimetric analysis

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